

PATENT SPECIFICATION

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 (72) Inventor CALVIN JOSEPH WORRELL



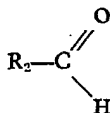
(54) IMPROVED GASOLINE COMPOSITIONS AND CLEANLINESS ADDITIVES THEREFOR

(71) We, ETHYL CORPORATION, a Corporation organised and existing under the Laws of the State of Virginia, United States of America, of 330 South Fourth Street, Richmond, State of Virginia, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to improved gasoline compositions for internal combustion engines and to gasoline additive concentrates therefor which provide cleaning of the induction system during engine operation.

Operation of an internal combustion engine over an extended period of time leads to the formation of deposits in the fuel induction system such as the carburetor and around the intake valves. These deposits interfere with the efficient operation of the engine and can lead to lower mileage and increased exhaust emissions. In the past, intake system cleanliness has been improved by use of gasoline containing imidazolines and hydrocarbyl amines.

According to the present invention there is provided a gasoline composition, which composition comprises a liquid hydrocarbon fuel of the gasoline boiling range and from 2.5 to 2000 ppm of a detergent additive which is the reaction product of a phenol, an aldehyde of the formula



wherein R₂ is hydrogen or alkyl, e.g. C₁ to C₆ alkyl and an amine having at least one H—N< group. The molal proportions of

phenol to aldehyde to amine can conveniently be 1:1 to 5:0.5 to 5.

The effectiveness of these additives in maintaining induction system cleanliness is surprising, because in the past such materials have been considered too high in molecular weight to have satisfactory inductibility and have only found use as sludge dispersants in lubricating oils (see, for example, U.S. Specifications Nos. 3,368,972 and 3,413,347).

The detergent additives have been found to be effective in quite low (detergent) concentrations in gasolines. Thus, the detergent additives are provided in concentrations of from 2.5 to 2000 ppm (ppm herein means parts by million by weight) with a preferred range being 3 to 1000 ppm, more preferably 6 to 100 ppm, and most preferably 12 to 50 ppm.

The detergent additive can be combined with any of most of the commercial gasolines, viz. liquid hydrocarbon fuels having a boiling range of from 80° F. to 430° F. As is known, such fuels are mixtures of hydrocarbons including aromatic, olefinic and saturated hydrocarbons. Preferred gasolines are those having a Research Octane Number of at least 85, and more preferably 90 or greater. Gasolines for which the additive is quite desirable are those having from 10 to 60 volume percent aromatic hydrocarbons, from 0 to 30 volume percent olefinic hydrocarbons and from 40 to 80 volume percent saturated hydrocarbons. The compositions of examples of base fuels suitable for use in the present invention are given in Table 1 below.

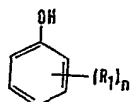
Desirably, the fuel will contain not more than about 0.1 weight percent sulphur, most preferably not more than about 0.02 weight percent sulphur, since sulphur components are undesirable as contributants to smog and other forms of atmospheric pollution.

TABLE 1
Hydrocarbon Blends of Particularly Preferred Base Fuels

| Fuel | Volume Percentage | | |
|------|-------------------|---------|-----------|
| | Aromatics | Olefins | Saturates |
| A | 35.0 | 2.0 | 63.0 |
| B | 40.0 | 1.5 | 58.6 |
| C | 40.0 | 2.0 | 58.0 |
| D | 33.5 | 1.0 | 65.5 |
| E | 36.5 | 2.5 | 61.0 |
| F | 43.5 | 1.5 | 55.0 |
| G | 49.5 | 2.5 | 48.0 |

For making the detergent additives, the preferred aldehyde reactant is formaldehyde which can be used in a monomeric or polymeric form such as paraformaldehyde.

The phenolic reactant is preferably an alkylphenol having the formula:



wherein n is 1 or 2, and R_1 is an aliphatic hydrocarbon group having an average molecular weight of from 400 to 1500. In a more preferred alkylphenol reactant the alkyl group has an average molecular weight of from 800 to 1300, and in the most preferred alkylphenols the alkyl group has an average molecular weight of from 900 to 1100.

The preferred alkylphenols can be readily made by known methods. An established method is the acid catalysed alkylation of phenol, in which a small amount of an acid catalyst such as sulphuric or phosphoric can be used. Alternatively, a Lewis acid such as BF_3 -etherate, BF_3 -phenate complex or



is added to the phenol and the olefin then added to the phenol at temperatures ranging from 0° up to 200° C. A preferred temperature range for this alkylation is from 25° to 150° C., and the most preferred range is from 50° to 100° C. The alkylation is readily carried out at atmospheric pressures, but if higher temperatures are employed the alkylation may be carried out at super atmospheric pressures up to about 1000 psig.

The alkylation of phenols produces a mixture of mono-, di- and tri-alkylated phenols. Although the preferred reactants are the mono-alkylated phenols, the alkylation mixture can be used without removing the higher alkylation products. The alkylation mixture formed by alkylating phenol with an olefin using an acid catalyst can be merely water washed to remove the unalkylated phenol and the acid catalyst and then used in the condensation reaction without removing the di- and tri-alkylated phenol products. The di-alkylated phenol enters into the condensation reaction and yields useful gasoline detergents. Another method of removing the unreacted phenol is to distill it out, preferably using steam distillation or under vacuum, after washing out the alkylation catalyst. The amount of di and tri-alkylated phenols can be kept to a minimum by restricting the amount of olefin reactant added to the phenol. Good results are obtained when the mole ratio of olefin to phenol is from 0.25 moles of olefin per mole of phenol to 1.0 mole of olefin per mole of phenol. A more preferred ratio is from 0.33 to 0.9, and a most preferred ratio is from 0.5 to 0.67 moles of olefin per mole of phenol.

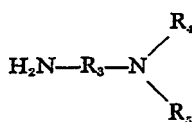
The olefin reactant used to alkylate the phenol is preferably a monoolefin with an average molecular weight of from 400 to 1500. The more preferred olefins are those formed from the polymerization of low molecular weight olefins containing from 2 to 10 carbon atoms, such as ethylene, propylene, butylene, pentene and decene. These result in polyalkene substituted phenols. A most preferred olefin is that made by the polymerization of propylene or butene to produce a polypropylene or polybutene mixture with an average molecular weight of from 900 to 1100. This gives

the highly preferred polypropylene and polybutene substituted phenols.

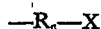
The amine reactants employed are those that have at least one active hydrogen bonded to an amino nitrogen atom, such that they can partake in a Mannich type condensation. Thus, primary and secondary amines are suitable, e.g. methyl amine and dimethyl amine.

Another class of suitable amine reactants are the N-substituted compounds such as the N-alkyl imidazolines and pyrimidines. Aromatic amines, with a reactive hydrogen atom attached to the nitrogen, are suitable, including, for example, aniline and meta and para phenylene diamines. The necessary amine reactive grouping is also found in secondary heterocyclic amines such as morpholine and indole.

Diamine compounds of the type represented by the formula



wherein R_3 is a divalent alkylene group, e.g. one having from 1 to 6 carbon atoms, and R_4 and R_5 can be alkyl groups, e.g. those having from 1 to 6 carbon atoms, or a group of the formula



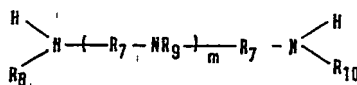
wherein R_6 is a divalent alkylene group, e.g. one having from 1 to 6 carbon atoms, and X is a hydroxyl or an amine group.

The two amine groups of such compounds can be bonded to the same or different carbon atoms. Thus, N_2N - dialkyl - methylenediamine, N_2N - dialkanol - 1,3 - ethanediamine, and N_2N - di(aminoalkyl) - 2,2 - propanediamine are illustrative of compounds in which the amine groups are attached to the same carbon atom.

Some examples of diamine reactants in which the amine groups are bonded to adjacent carbon atoms of the R_3 alkylene group are N_2N - dialkyl - 1,2 - ethylenediamine, N_2N - dialkanol - 1,2 - propanediamine, N_2N - di(aminoalkyl) - 2,3 - butanediamine, and N_2N - dialkyl - 2,3,4 - (4 - methylpentane)diamine.

Some examples of diamine reactants in which the amine groups are bonded to carbon atoms on the alkylene group represented by R_3 which are removed from each other by one or more intervening carbon atoms are N_2N - dialkyl - 1,3 - propanediamine e.g. N_2N - dimethyl - 1,3 - propanediamine, N_2N - dialkanol - 1,3 - butanediamine, N_2N - di(aminoalkyl) - 1,4 - butanediamine, and N_2N - dialkyl - 1,3 - hexanediamine.

Alkylene polyamines, for example, those of the formula:

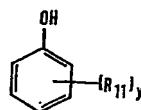


wherein R_8 , R_9 and R_{10} are hydrogen or an alkyl group having from 1 to 4 carbon atoms, and R_7 is a divalent saturated aliphatic hydrocarbon group having from 2 to 4 carbon atoms and m is 0 or an integer of from 1 to 4 are another useful class of reactants.

Preferred alkylene polyamines are the ethylene polyamines e.g. ethylene diamine, diethylene triamine, tetraethylene pentamine and mixtures thereof, although other alkylene polyamines such as tributyltetramine may be used if desired.

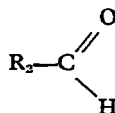
In an alternative the detergent additives may be the reaction product of:

- (i) one mole of phenol or a lower (C_2-C_4) alkyl phenol having the formula



wherein y is 1 or 2, and R_{11} is lower (C_2-C_4) alkyl;

- (ii) from 1 to 3 moles of an aldehyde having the formula



- wherein R_2 is hydrogen or an alkyl group having from 1 to 6 carbon atoms; and (iii) from 0.5 to 3 moles of an amine having at least one



wherein R_{12} is an alkyl group having 30 or more carbon atoms.

In this alternative the amine may be a monoamine or a polyamine. Typically the amine may be derived from a polymer of a C_2 to C_4 monomer e.g. polypropylene or polybutene, and the polymer may have an average molecular weight of 400 to 1500.

The detergent additives are easily prepared by mixing together the phenol reactant, the aldehyde reactant and the amine reactant, and heating them to a temperature sufficient to cause the reaction to occur. The reaction may be carried out without any solvent, but

the use of a solvent is usually preferred. Preferred solvents are the water-immiscible solvents including water-insoluble alcohols (e.g. amyl alcohol) and hydrocarbons. The more preferred water-immiscible solvents are hydrocarbon solvents boiling from 50° to about 200° C. Highly preferred solvents are the aromatic hydrocarbon solvents such as benzene, toluene and xylene. Of these, the most preferred solvent is toluene. The amount of solvent employed is not critical. Good results are obtained when from one to about 50 percent of the reaction mass is solvent. A more preferred quantity is from 3 to about 25 percent, and a most preferred quantity of solvent is from 5 to 10 percent.

The ratio of reactants per mole of alkylphenol can vary from 1 to 5 e.g. 1 to 3, moles of aldehyde reactant and from 0.5 to 5 e.g. 0.5 to 3, moles of amine reactant. Molar amounts of amine less than one can be used when the amine contains more than one H—N< group, such as in the ethylene polyamines (e.g. tetraethylene-pentamine). A more preferred reactant ratio based on one mole of alkylphenol is from 2.5 to 4 moles of aldehyde and from 1.5 to 2.5 moles of amine reactant. A most preferred ratio of reactant is about 2 moles of alkylphenol to about 3 moles of aldehyde to about 2 moles of amine reactant. This ratio gives an especially useful product when the alkylphenol is a polybutene-substituted phenol in which the polybutene group has a molecular weight of 900 to 1100, the aldehyde is formaldehyde and the amine is N,N - dimethyl - 1,3-propanediamine.

The reaction will proceed at temperatures ranging from 50° to 200° C. A more preferred temperature range is from 75° to 175° C. When a solvent is employed it is desirable to conduct the reaction at the reflux temperature of the solvent-containing reaction mass. For example, when toluene is used as the solvent, the condensation proceeds at 100° to 150° C. as the water formed in the reaction is removed. The water formed in the reaction co-distills together with the water-immiscible solvent, permitting its removal from the reaction zone. During water removal the water-immiscible solvent is returned to the reaction zone after separating water from it.

The time required to complete the reaction depends upon the reactants employed and the reaction temperature used. Under most conditions the reactions is complete in from one to 8 hours.

The reaction product is a viscous oil and is usually diluted with a neutral oil to aid in handling. A particularly useful mixture is about two-thirds condensation product and one-third neutral oil.

The following examples illustrate the preparation of detergent additives for use in the

present invention. All parts are parts by weight unless otherwise indicated.

EXAMPLE 1.

To a reaction vessel equipped with a stirrer, condenser and thermometer were added 363 parts of polybutene having an average molecular weight of 1100 and 94 parts of phenol. Over a period of 3 hours, 14.2 parts of a BF₃-etherate complex were added while maintaining the reaction temperature between 50° and 60° C. The reaction mixture was then stirred at 55° to 60° C. for an additional 4.5 hours and then transferred to a second reaction vessel containing 750 parts of water. The aqueous phase was removed and the organic phase washed 4 times with 250 parts of water at 60° C., removing the aqueous phase after each wash. The organic product was then diluted with about 200 parts of *n*-hexane and dried with anhydrous sodium sulphate. Next the product was filtered and the hexane and other volatiles removed by vacuum distillation until the product remaining was at 75° C. at 0.3 mm Hg. As a reaction product, there was obtained 368.9 parts of an alkylphenol as a viscous amber-coloured oil having an average molecular weight of 810.

In a separate reaction vessel were placed 267 parts of the alkylphenol as prepared above, 33.6 parts of N,N - dimethyl - 1,3 - propanediamine and 330 parts of isopropanol. While stirring, 15.8 parts of 95 per cent paraformaldehyde were added. The reaction mixture was then refluxed for 6.5 hours. Following this, the solvent and other volatiles were distilled out at a reaction mass temperature of 115° C. and at about 15 mm Hg. The reaction mass was a viscous amber-coloured liquid having excellent detergent action in fuel induction systems.

EXAMPLE 2.

To a reaction vessel equipped with a stirrer, condenser and thermometer were added 934 parts of a polybutene having an average molecular weight of about 900, 196 parts of phenol and 22 parts of a BF₃-ether complex containing 48 per cent BF₃. The temperature was raised to 60° C. and maintained there for 3 hours, following which 120 parts of water were added. Steam was then injected into the reaction mass, causing the unalkylated phenol to distill out. The steam distillation was continued until almost all the phenol had been removed. About 870 parts of toluene were then added and the organic phase separated and dried over anhydrous sodium sulphate. The toluene was then removed by vacuum distillation until the alkylated phenol reached a temperature of 145° C. at a pressure of 0.2 mm Hg. Infrared analysis for hydroxyl content showed that the product had an average molecular weight of 1060.

To a second reaction vessel equipped with stirrer, condenser and thermometer were added 313 parts of the alkylphenol prepared above, 30.1 parts of N,N-dimethyl-1,3-propanediamine, 14 parts of 95 per cent paraformaldehyde and 152 parts of toluene. While stirring, the reaction temperature was raised gradually to 145° C. over a 2.5 hour period. Water was separated from the toluene that distilled out and the toluene distillate was returned to the reaction zone. The volatile material in the reaction product was then removed by maintaining the product at about 140° to 145° C. while reducing the pressure in the reaction system to about 12 mm Hg. The volatiles that distilled out during this period were condensed and removed from the reaction mass, resulting in 352 parts of the condensation product in the form of a viscous oil.

EXAMPLE 3.

To a reaction vessel equipped as in Example 1 were added 260 parts of isopropyl alcohol, 266 parts (0.33 mole) of the alkylphenol prepared as described in Example 1 and 45 parts (0.33 mole) of N,N-di(2-hydroxyethyl)-1,3-propanediamine. While stirring, 15.8 parts (0.5 mole) of 95 per cent paraformaldehyde were added. The reaction mixture was stirred at reflux for 6.5 hours, following which the solvent and volatiles were distilled out at a liquid temperature of 115° C. and at 15 mm. Hg., leaving a viscous gasoline soluble residue.

EXAMPLE 4.

(i) Preparation of Alkylated Phenol

A reaction vessel was charged with 56.0 parts of a commercial polybutylene (average molecular weight about 900), 8.6 parts of pre-melted phenol and 20.0 parts of n-heptane. The reaction mass was stirred, heated to 33° C., and then 2.39 parts of BF₃-phenol complex were added over a 16 minute period. The temperature of the reaction mass rose to 49° C. and the mass was stirred under nitrogen for an additional 49 minutes at temperatures ranging from 49° to 51° C.

The reaction was quenched by added 16.5 parts of methanol followed by 9.38 parts of aqueous ammonia to the reaction vessel. Stirring was discontinued and the reaction mass was allowed to separate into two layers. The lower layer was then drawn off and discarded. The alkylated phenol layer remaining in the reaction vessel was washed first with 16.68 parts of water and then a second time with 16.5 parts of methanol and 12.5 parts of water.

(ii) Preparation of Phenol/CH₂O/Amine Condensation Product

To the washed alkylated phenol product from (i) were added 6.44 parts of N,N-di-

methyl-1,3-propane-diamine and 3.03 parts of 91 percent paraformaldehyde. The reaction mixture was heated to 35° to 37° C. and stirred at this temperature for 35 minutes. The reaction mixture was then heated with stirring, to 129° C. and held at 129° to 131° C. for two hours. During this heating cycle, water and heptane were distilled off. A sample of the reaction product was taken at this point and labeled Example 4—A product.

About 10 parts of n-heptane were then added to the reaction mixture and the resulting mixture was allowed to cool to about room temperature. This reaction mixture was then heated to 193° C. to 202° C. and maintained with stirring at this temperature for 3 hours and 15 minutes. The solvent was vacuum stripped during the latter portion of this three-hour heating cycle. The reaction mixture was then allowed to cool to 114° C. at which point 33.8 parts of xylene were added. This mixture was stirred and allowed to cool to about room temperature.

The diluted product was then filtered, yielding 88.51 parts of a honey-coloured, fluid reaction product. This product was labelled Example 4—B product.

The Example 4—A product had an average molecular weight of 1128 and contained 2.44 percent of basic nitrogen. The Example 4—B product was analyzed after stripping the xylene and this product had a number average molecular weight of 1508 and contained 2.02 percent (82 percent of theory) basic nitrogen.

Detergent materials manufactured as described and as exemplified above are highly effective additives to gasoline for cleanliness purposes, as is shown hereinafter. It has also been found that the further addition to the gasoline, in addition to the detergent additive, of a small amount of mineral oil is highly advantageous in combination, particularly in promoting the cleaning of intake valves and stems. The oil added for this embodiment can be provided in proportions of about 0.05 to about 0.5 volume percent based on the final gasolines. The more preferred oils are naphthenic oils but the use of these is not absolutely essential. The mineral oils used will have a viscosity of about 70 to 2000 SUS at 100° F.

In an additional preferred embodiment a synthetic olefin oligomer is used (see co-pending Application Serial No. 1,325,701) in place of or together with the mineral oil adjuvant. These materials are prepared by the polymerization of aliphatic monoolefinic hydrocarbons such as ethylene, propylene and decene-1 or mixtures of hydrocarbons as discussed below. The oligomer can be prepared under the influence of catalysts such as the Lewis acid type, including, for example, aluminum chloride or boron trichloride as well as the metal alkyl types of catalysts such as tri-

ethyl aluminium, diethyl aluminium chloride, methyl aluminium sesquichloride and diethyl zinc. The catalyst can be used alone or in combination with other materials. Thus, a metal salt modifier such as titanium tetrachloride or cobalt iodide can be provided in addition to a metal alkyl catalyst.

The products of the polymerization are desirably normally liquid oligomers with an average molecular weight of 300 to 2000, especially 350 to 1500. Highly desirable oligomers of this character can be obtained by the polymerization of mixtures of olefins. One such mixture is of aliphatic monoolefins with at least 12 carbon atoms, preferably of from 12 to 32 carbon atoms and consisting predominantly of alpha olefins. Mixtures such

as these can be polymerized at 20° C. to 120° C., preferably 40° C. to 110° C. An aluminium halide catalyst in the absence of any lower alkyl monohalide compound is preferred.

Olefin mixtures of the above kind are available by known processes. For example, they can be derived by cracking wax range paraffins, or by polymerizing low molecular weight monoolefins such as ethylene. Such mixtures can contain vinylidene or internal olefin components, as well as paraffin compounds in the indicated molecular weight range. The following Table 2 gives illustrative compositions of olefin mixtures of the "C₁₂₊" type, viz., predominating in olefins of the C₁₂ to C₃₀ molecular weight range:

TABLE 2
C₁₂₊ Monoolefin Mixtures % By Weight ⁽¹⁾

| Olefin Carbon No. | A | B | C | C' ⁽⁴⁾ |
|--|-----------------------|-------|--------|-------------------|
| C ₈ —C ₁₀ | 1.84 | 1.40 | 2.01 | 4.35 |
| C ₁₂ | 20.39 | 16.72 | 19.40 | 13.92 |
| C ₁₄ | 12.15 | 9.76 | 12.59 | 9.91 |
| C ₁₆ | 10.65 | 8.28 | 10.97 | 9.27 |
| C ₁₈ | 6.29 | 6.34 | 8.88 | 9.51 |
| C ₂₀ | 4.35 | 4.43 | 5.15 | 6.04 |
| C ₂₂ | 3.25 | 5.59 | 6.63 | 7.51 |
| C ₂₄ | 4.38 | 7.50 | 7.70 | 8.21 |
| C ₂₆ | 3.51 | 6.41 | 4.78 | 5.80 |
| C ₂₈ | 2.07 | 3.69 | 2.40 | 3.00 |
| C ₃₀ | 1.33 | 1.25 | 0.90 | 0.61 |
| C ₃₂ | — | 0.38 | 0.17 | — |
| C ₃₄ | — | 0.08 | — | — |
| Total Olefins | 70.21% | 72% | 81.58% | 78.13% |
| Total Paraffins | 18.30% | 28% | 18.42% | 21.87% |
| Other By-Products | 11.49% ⁽²⁾ | — | — | — |
| Olefin Configuration % Distribution ⁽³⁾ | | | | |
| α | 69.7% | 60.6% | — | 60.1% |
| Internal | 30.3% | 39.3% | — | 39.9% |

⁽¹⁾ Vapour phase chromatographic analysis

⁽²⁾ Estimated

⁽³⁾ Nuclear magnetic resonance analysis

⁽⁴⁾ For this mixture, VPC analysis was based on 91.11% recovered normalized. The mixture also contained by-product alcohols.

Another group of desirable olefin mixtures of such mixtures are given in the following are C_{14+} olefin mixtures, and typical analyses Table 3.

TABLE 3

 C_{14+} Monoolefin Mixtures

| Olefin Carbon No. | D | E | F |
|--------------------------------------|-------|------|-----|
| C_{12} | 0.1 | 0.3 | 3 |
| C_{14} | 10.4 | 26.5 | 25 |
| C_{16} | 23.3 | 58.0 | 30 |
| C_{18} | 18.3 | 12.9 | 15 |
| C_{20} | 8.5 | — | 8 |
| C_{22} | 8.6 | — | 6 |
| C_{24} | 11.4 | — | 5 |
| C_{26} | 9.9 | — | 3 |
| C_{28} | 5.7 | — | 2 |
| C_{30} | 2.8 | — | 2 |
| C_{32} | 1.0 | — | 1 |
| Olefin Configuration | | | |
| α { Vinyl | 31.6% | — | — |
| | 29.7% | 50% | 50% |
| Internal | 22.8% | — | — |
| Non-olefin components ⁽¹⁾ | 15.9% | 2.3% | 12% |

(i) By-product paraffins and alkanols

Further and more preferred monoolefin mixtures suitable for oligomerization contain predominantly α -monoolefins of even carbon number ranging from C_{18} to C_{28+} . Again, small amounts of olefin outside this range as well as by-products can also be present. These pre-

ferred monoolefin mixtures will be referred to as C_{18+} monoolefins or C_{18+} monoolefin mixtures. A general composition range of these C_{18+} monoolefins is set out in the following Table 4.

TABLE 4

C₁₈₊ Monoolefin Composition Range

| Olefin Carbon No. | Percent by Weight (1) |
|---|-----------------------|
| C ₁₆₋ ⁽²⁾ | 0 — 6 |
| C ₁₈ | 0.5—22 |
| C ₂₀ | 32 —55 |
| C ₂₂ | 18 —39 |
| C ₂₄ | 6 —16 |
| C ₂₆ | 0.5— 8 |
| C ₂₈₊ ⁽³⁾ | 0 —10 |
| Paraffins | 0 —10 |
| Olefin Configuration Percent Distribution ⁽⁴⁾ | |
| α { Vinyl | 30 —55 |
| { Vinylidene | 0 —55 |
| Internal | 10 —70 |

⁽¹⁾ Vapour phase chromatographic (VPC) analysis.

⁽²⁾ C₁₆₊ includes C₁₆ and lower olefins; but essentially no olefins lower than about C₁₂.

⁽³⁾ C₂₈₊ includes C₂₈ and higher olefins.

⁽⁴⁾ Nuclear magnetic resonance (NMR) analysis.

Specific examples of C_{18+} monoolefin compositions are given in the following Table 5.

TABLE 5

C_{18+} Monoolefin Mixtures % By Weight ⁽¹⁾

| Olefin Carbon No. | G | H | I | J | K | L | M | N |
|--|-------|-------|-------|-------|-------|-------|------|-------------------|
| C_{16-} | — | — | 0.17 | 0.08 | 0.08 | 0.41 | 3.0 | 11 |
| C_{18} | 5.06 | 0.50 | 9.50 | 6.19 | 4.34 | 10.83 | 16.7 | 63 |
| C_{20} | 50.12 | 42.66 | 47.69 | 45.79 | 49.31 | 41.06 | 33.2 | 20 |
| C_{22} | 28.55 | 37.10 | 26.85 | 29.58 | 30.31 | 24.42 | 19.6 | 6 |
| C_{24} | 11.33 | 14.38 | 11.19 | 13.56 | 11.75 | 11.56 | 13.2 | — |
| C_{26} | 4.22 | 0.80 | 13.54 | 4.13 | 2.97 | 4.16 | 6.3 | — |
| C_{28} | 0.72 | — | 0.87 | 0.66 | 0.91 | 0.94 | 7.9 | — |
| C_{30} | — | — | 0.19 | 0.01 | 0.28 | — | — | — |
| C_{32} | — | — | — | — | 0.05 | — | — | — |
| Paraffin | — | — | — | — | — | 5.07 | 3.8 | — |
| Olefin Configuration % Distribution ⁽²⁾ | | | | | | | | |
| α { Vinyl | 50.8 | — | 54.0 | 43.3 | 37.7 | 47.4 | 32.2 | 45 ⁽³⁾ |
| Vinylidene | 35.5 | — | 34.0 | 41.5 | 46.7 | 32.2 | 37.3 | 45 ⁽³⁾ |
| Internal | 13.8 | — | 12.0 | 15.4 | 15.6 | 20.4 | 30.4 | 10 ⁽³⁾ |

⁽¹⁾ Vapour phase chromatographic analysis

⁽²⁾ Nuclear magnetic resonance analysis

⁽³⁾ Estimated

The more preferred monoolefin mixtures can also be treated with an isomerization catalyst prior to being polymerized. The isomerization effected in this case is primarily isomerization of the vinylidene type α -olefins to internal olefins. Thus, for example, by isomerizing a more preferred C_{12+} olefin mixture containing 30% vinyl α -olefins, 40% vinylidene α -olefins, and 30% internal olefins using a suitable catalyst such as silica gel or activated alumina, the olefin mixture can be converted to a mixture containing 30% vinyl α -olefins, less than 40% vinylidene α -olefins and 30% + internal olefins, the "+" indicating the amount of vinylidene olefin isomerized to internal olefin. Depending on the extent of vinylidene olefin isomerization, the resulting isomerized monoolefin mixture may contain (a) α -olefins predominantly, (b) internal olefins predominantly, or (c) an equal amount of α -olefins and internal olefins.

The following examples illustrate the preparation of preferred normally liquid olefin

hydrocarbons having a molecular weight of from 350 to 1500 by Friedel-Crafts polymerization of mixtures of α -monoolefins of the type described above. All parts are by weight unless otherwise indicated. The molecular weights of the olefin hydrocarbon products were determined by vapor phase osmometry.

EXAMPLE 5.

A vessel was charged with 383 parts of a C_{18+} monoolefin mixture. To this olefin mixture were added 20 parts of aluminium chloride, gradually, over a 25-minute period. The vessel was cooled during the addition of the aluminium chloride in order to maintain the temperature of the reaction mixture at less than about 50° C. After the addition of the aluminium chloride was completed, the mixture was heated with stirring at 95° C. for 2 hours. Then, about 100 parts of a 10% HCl solution were added to quench the catalyst. The reaction mixture was then diluted with hexane (to facilitate handling) and washed

with water until the washings were free from acid. The reaction mixture was then filtered through Celite. The filtrate was stripped of water and solvent under vacuum on a steam bath. The product obtained was 320 parts of a clear yellow slightly viscous liquid. The infrared spectrum of this product indicated it to be a polymerized hydrocarbon. The molecular weight was 818.

EXAMPLE 6.

A vessel was flushed with nitrogen and then charged with 454 parts of a C_{12+} monoolefin mixture. The olefin mixture was cooled to 15°C . and 15 parts of aluminium chloride were added over a 3 to 4 minute period. The reaction mixture was then heated with stirring at 70°C . for 2 hours. The catalyst was next quenched by adding about 150 parts of a 10% HCl solution to the mixture. About 350 parts of hexane were added (to facilitate handling) and the diluted mixture was washed with water until the washings were acid free. The reaction mixture was then filtered through Celite. The filtrate was stripped of water and solvent under vacuum on a steam bath. The product obtained was 308 parts of a clear, yellow, very fluid liquid. The molecular weight of this product was 368.

EXAMPLE 7.

A vessel was charged with 589 parts of a C_{12+} monoolefin mixture and 16.8 parts of aluminium chloride were added over a 6-minute period. The mixture was then heated with stirring at 110°C . for 3 hours, cooled, diluted with hexane and treated with about 200 parts of a 10% HCl solution. The reaction mixture was next washed with water until the washings were free from acid and then filtered. The filtrate was stripped of water and solvent under vacuum to yield 509 parts of a clear, yellow, liquid product. The molecular weight of this product was 378.

A similar reaction is obtained when a C_{14+} monoolefin mixture is used in place of the C_{12+} mixture of Example 7.

EXAMPLE 8.

A mixture of 400 parts of a C_{12+} monoolefin mixture and 400 parts of a C_{18+} monoolefin mixture was charged to a flask and cooled to 20°C . This mixture of monoolefins was treated with 40 parts of aluminium chloride, added gradually over a 72-minute period. During the addition of aluminium chloride, the temperature was maintained at 21°C . The reaction was continued with stirring at 22°C . to 30°C . for 4 hours. The reaction mixture was then diluted with about 175 parts of hexane and treated with about 200 parts of a 10% HCl solution. The mixture was then washed with water until acid free. It was filtered through Celite and the filtrate was stripped of solvent and water under

vacuum. The product obtained was 696 parts of a clear, yellow liquid having a molecular weight of 623.

EXAMPLE 9.

A vessel was charged with 600 parts of a C_{12+} monoolefin mixture. To this olefin mixture were added 17.1 parts of aluminium chloride, gradually, over a 35-minute period. The temperature during this addition ranged from 20° to 23°C . The reaction was continued with stirring at 23°C . for $3\frac{3}{4}$ hours. The mixture was then diluted with about 175 parts of hexane and treated with about 250 parts of a 10 percent HCl solution. The mixture was next washed with water until acid free and then filtered through Celite. The filtrate was stripped under vacuum to yield 519 parts of a clear, yellow liquid product having a molecular weight of 366.

In another run, 877 parts of a predominantly α , $C_{18}-C_{28}$ range monoolefin mixture was polymerized using 75 parts of AlCl_3 at 70°C . for 2 hours to produce a useful polyolefin additive.

Analogous results are obtained in Example 9 when 12 parts of aluminium chloride, or 12 parts of aluminium bromide, are used as the catalyst; or when the C_{12+} monoolefin mixture is isomerized by contacting the mixture with silica gel for a short period of time.

Tests have been carried out which demonstrate the detergent properties of the compositions of the present invention. These tests show the compositions to be effective not only in cleaning carburetors, but also in removing intake valve deposits. An important feature here is that the additives not only prevent the formation of deposits in clean systems, but will actually remove deposits already present in dirty induction systems. This latter effect is especially important because the compositions can beneficially be used in automotive engines that have already accumulated deposits and thereby the deposits will be removed, resulting in more efficient engine operation and better durability.

Additionally, the use of the compositions of the present invention also has a beneficial effect in the engine crankcase.

Carburetor Detergency Tests

The carburetor of a standard 6-cylinder engine is fitted with a weighed split removable internal throttle-body sleeve. The engine is then operated on a cycle of 5 minutes idle, followed by 70-second part-throttle operation for a total of 2 hours. Blow-by is recycled through the carburetor. Following the test, the sleeve is removed and weighed. Results are reported in terms of percent reduction in deposits compared to that accumulated during operation of the engine for the same length of time but without the test additive.

The results of the carburetor detergency

test employing the detergent of Example 2 is shown in the following table.

| | Concentration (1) | % Deposit Reduction |
|---|-------------------|---------------------|
| | 30 ppm | 54 |
| 5 | 63 ppm | 73 |

(1) Additive concentrate containing Example 2:75 SUS hydrocarbon oil in a weight ratio of about 2:1.

As these results show, the use of the detergent of Example 2 leads to a 54 percent reduction in carburetor deposits employing a concentration of only 30 ppm. At 63 ppm, a reduction of 73 percent was observed.

The mineral oil and polyolefin adjuvants

previously described for use in combination with the detergent additives of this invention function mainly in the area of the intake manifold and intake valves. Use of these materials alone may result in slightly more carburetor deposits. However, when used in combination with the detergent additives of this invention, carburetor cleanliness is maintained, as shown by the following results obtained using the previous carburetor detergency test, in which the fuel contained an adjuvant amount of a polyolefin prepared as described in Example 6 except that it had an average molecular weight of 495. In the first test the polyolefin was used alone, and in the second test it was used in combination with the detergent of Example 2 (containing about 33% by weight of a 75 SUS hydrocarbon oil).

| | Additive | % Deposit Reduction |
|----|--|---------------------|
| | polyolefin (2000 ppm) alone | 11.5% gain |
| 35 | polyolefin (2000 ppm) plus detergent of Example 2 (63 ppm) | 73% |

As the above results show, even though the polyolefin alone leads to a slight increase in carburetor deposits, this increase is readily offset by the presence of the detergent of Example 2. In fact, the percent deposit reduction at 63 ppm was 73 percent, which is as good as that obtained with the same amount of the same detergent in the absence of the polyolefin.

The results of the carburetor detergency test employing the detergents of Example 4, alone and in combination with an adjuvant amount of a polyolefin (having an average molecular weight of 470) prepared using substantially the procedure described in Example 6, were as follows:

| Test | Additive | Concentration (ppm) | Deposit Reduction |
|------|-----------------------------|---------------------|--------------------|
| 1 | Example 4-A ⁽¹⁾ | 27 | 62% ⁽²⁾ |
| 2 | Example 4-B | 21 | 55% ⁽²⁾ |
| 3 | Example 4-B | 10 | 55% ⁽²⁾ |
| 4 | Example 4-B + polyolefin | 20 400 | 59% |
| 5 | Example 4-B + polyolefin | 50 400 | 52% |
| 6 | Example 4-B + polyolefin | 10 400 | 51% ⁽²⁾ |

⁽¹⁾ Diluted with xylene (2 parts Example 4-A product: about 1 part xylene)

⁽²⁾ Average of two runs

The above data clearly show the effectiveness of the present detergent additives in varying concentrations as carburetor detergents, either alone or in combination with an adjuvant.

Intake Valve Clean-Up Test

A standard 6-cylinder automotive engine is operated for 30 hours on a cycle known to

cause severe intake valve deposit formation. The cycle consists of running the engine 150 seconds at 2000 rpm, followed by 40 seconds at 500 rpm. The fuel is a commercial gasoline containing 3 grams of lead per gallon as a commercial tetraethyllead antiknock fluid. At the end of the 30 hours the intake valves are removed and weighed. The engine is then reassembled and run for an additional 30 hours

5 using the same cycle and using the same fuel except containing the additive under test. The valves are again removed and weighed. Results are reported in terms of percent reduction in intake valve deposits due to the additive.

The following results were obtained in three tests employing a polyolefin adjuvant alone and in combination with an additive of the present invention as indicated.

10

| Additive | Conc. (ppm) | % Clean-up |
|--|--------------|------------|
| polyolefin of Example 6 | 1000 | 61 |
| polyolefin of Example 6 detergent of Example 2* | 1000 250 | 73 |
| polyolefin of Example 6 detergent of Example 2* | 1000 1000 | 87 |

* concentrate containing 2 parts Example 2 additive; 1 part 75 SUS oil

15 As the above results show, although the polyolefin was fairly effective in cleaning deposit-laden intake valves, its effectiveness was significantly increased by use of the detergent additive. The net result is that the detergent additive of this invention provides a means of not only maintaining a clean carburetor, but also functions to maintain a clean induction system and, in fact, when used with an engine that has already accumulated induction system deposits, the additive provides a means of cleaning up these deposits. The overall result is that the entire fuel induction system is maintained much cleaner, providing more efficient engine operation.

Engine Crankcase Deposits

The CRC L-43 test is a single cylinder engine research technique used to study the low temperature deposit forming properties of engine crankcase lubricants. The L-43 test procedure provides that the engine be operated at constant speed and load, but with coolant temperature cycling. The lubricant's sludge and varnish forming tendencies are judged by visual observation of the amount of deposit found on certain engine parts after a given period of engine operation. Following are the results of L-43 tests showing the effect in the crankcase of gasoline containing a detergent additive of the present invention.

30

35

40

L-43 Deposit Rating

| Concentration of Example 4-B Additive in the Gasoline | None | 100 ppm |
|--|------|---------|
| Sludge⁽¹⁾ | | |
| Valve Cover | 5.7 | 8.0 |
| Push Rod Cover | 7.4 | 8.0 |
| Rocket Arm Assembly | 7.0 | 10.0 |
| Lower Cylinder | 5.3 | 10.0 |
| Timing Gear Cover | 6.7 | 10.0 |
| Average | 6.4 | 9.2 |
| Hours to 9.5 Average Sludge Rating | 86 | 116 |
| Varnish⁽¹⁾ | | |
| Valve Cover | 8.5 | 8.0 |
| Push Rod Cover | 8.0 | 8.0 |
| Crankcase Side Plate | 8.0 | 9.0 |
| Average | 8.1 | 8.3 |

⁽¹⁾ Rated after 120 hours of engine operation using Standard CRC rating procedure; 10=Clean

As the above data clearly show, the detergent additive used in the present invention also reduces the deposit build-up in parts of the engine other than the intake system and the carburetor. This is indicated by the reduced sludge rating for the run using gasoline containing 100 ppm of Example 4-B; and also by the greater amount of time (116 hours vs. 86 hours) required for deposits to form in the engine. Thus the additive of the present invention functions as a multi-purpose detergent additive.

The additives used in this invention can be added directly to gasoline or they can be added in the form of a concentrate. Thus, another embodiment of the invention is a gasoline additive concentrate, which concentrate comprises from 0.1 to 90 percent by weight of a detergent additive as described above and a diluent which is an aliphatic solvent, an aromatic solvent, or a normally liquid aliphatic hydrocarbon oligomer having a molecular weight of from 300 to 2000, or a mixture thereof. The amount of detergent in the concentrate can, for example, vary from 10 to 90 percent by weight. The diluent serves to maintain the concentrate in a liquid form making it easy to handle and to meter into gasoline blending systems. Preferred diluents

are hydrocarbons including both aliphatic and aromatic hydrocarbons such as hexane, heptane, octane, petroleum ether, kerosene, benzene, toluene and xylene, and mixtures thereof. Thus, the amount of detergent in the concentrate, using a preferred diluent, ranges from 19 to 90 percent by weight and preferably from 35 to 75 percent by weight. A more preferred diluent is a polyolefin oligomer as described above, which may be present in an amount of from 10 to 90 percent by weight. For example, the olefin oligomer component can be provided in the concentrate mix in proportions of 9 to 1/9 parts per part of the detergent additive, a more preferred ratio being from about 2 to 1/3 part per part of the detergent additive. The advantage of using such a higher boiling point hydrocarbon diluent is that it also serves as the previously-described polyolefin adjuvant. Thus, a more preferred concentrate contains from 0.1 to 75 percent by weight preferably 0.2 to 50 percent by weight, more preferably 0.3 to 35 percent by weight, and most preferably 1 to 20 percent by weights of the detergent in a polyolefin oligomer diluent of the above described type. When this concentrate is added to gasoline a fuel is provided which will maintain the entire induction system in a high degree of

cleanliness. Concentrates containing a combination of these detergents can also be used.

- Especially good results have been obtained when the hydrocarbon diluent employed in the concentrate is one of the previously-described polyolefin oligomers made by polymerizing an olefin or mixture of olefinic hydrocarbons containing about 12 or more carbon atoms, preferably from 12 to 32 carbon atoms, to produce a liquid olefin polymer having an average molecular weight of 300 to 1500.

- The detergent concentrate can contain other additives normally used with gasoline, forming an additive "package". For example, the concentrate can contain gasoline antioxidants such as 2,6 - di - *tert* - butylphenol, mixtures of butylated phenol containing, for example, about 75 percent of 2,6 - di - *tert* - butylphenol, 15 percent *o* - *tert* - butylphenol, N-isopropylphenylenediamine; phosphorus additives such as tricresylphosphate, trimethylphos-

phate, phenyldimethylphosphate, dimethylphenylphosphate and tris (β - chloropropyl)-phosphate; antiknock promoters such as *tert*-butyl acetate; de-icers such as methanol; isopropanol, *n*-butanol and isobutanol; tetraalkyllead antiknocks such as tetraethyllead; tetramethyllead and redistributed tetraethyltetramethyl lead; scavengers such as ethylene dichloride, ethylene dibromide and dibromobutanes; other antiknock agents such as methyl cyclopentadienyl manganese tricarbonyl, ferrocene, methyl ferrocene, cyclopentadienyl nickel nitrosyl and N-methylaniline; metal deactivators such as N,N' - disalicylidene - 1,2 - diamino propane; dyes; and corrosion inhibitors.

The concentrates of this invention are readily prepared by merely blending the ingredients until a homogenous solution is obtained. Illustrative blend compositions for concentrates are tabulated below.

TABLE 6

Additive Concentrate Mixtures

| Mix No. | Detergent component and quantity ¹ | Other components and quantities ¹ |
|---------|---|--|
| 1 | From Ex. 4, product 4B, 10 | C ₆ —C ₈ aromatic hydrocarbon mixture, 80. |
| 2 | 1 to 100 parts of 4B product | Oligomeric product of Example 6, 400. |

¹ Parts by weight.

The final gasoline for marketing and use are readily prepared by adding the detergent condensate material, to a base gasoline supply.

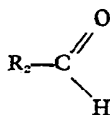
TABLE 7

Typical Formulations for Finished Gasolines

| Mix | Gasoline base stock and quantity, gal. | Additives |
|-----|--|--|
| I | A | 10,000 25 lb. detergent of Example 2, 100 lb. poly C ₁₈₊ olefin prepared as in Example 9, 96.5 tetraethyllead, plus 1 theory ethylene dichloride and 0.5 theory ethylene dibromide, 15.5 lb. trimethyl phosphate. |
| II | E | 10,000 2.5 detergent of Example 3, 50 lb. of neutral mineral oil, 100 SUS at 100°F. |
| III | B | 10,000 100 lb. of additive or concentrate mix 2 of Table 6, 84 lb. tetraethyllead as a commercial anti-knock fluid, and 4.8 lb. trimethyl phosphate. |
| IV | F | — 5 ppm of product of Example 2 and 1000 ppm of a polyolefin having an average molecular weight of 1500. |

WHAT WE CLAIM IS:—

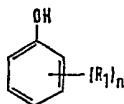
1. A gasoline composition, which comprises a liquid hydrocarbon fuel of the gasoline boiling range and from 2.5 to 2000 ppm of a detergent additive which is the reaction product of a phenol, an aldehyde of the formula



- 10 wherein R₂ is hydrogen or alkyl, and an amine having at least one H—N< group.

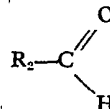
2. A composition as claimed in claim 1, wherein the detergent additive is the reaction product of:

- 15 (i) one mole part of an alkylphenol having the formula



- 20 wherein n is 1 or 2, and R₁ is an aliphatic hydrocarbon group having a molecular weight of from 400 to 1500;

- (ii) from 1 to 5 mole parts of an aldehyde having the formula:



wherein R₂ is hydrogen or an alkyl group having from 1 to 6 carbon atoms; and 25

- (iii) from 0.5 to 5 mole parts of an amine having at least one H—N< group.

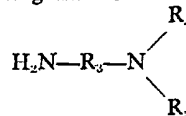
3. A composition as claimed in claim 2, wherein R₁ is a polyalkene group having a molecular weight of from 800 to 1300. 30

4. A composition as claimed in claim 3, wherein the polyalkene group has a molecular weight of from 900 to 1100.

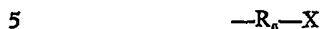
5. A composition as claimed in any one of claims 2 to 4, wherein R₁ is a polybutene group. 35

6. A composition as claimed in any one of claims 2 to 4, wherein R₁ is a polypropylene group.

7. A composition as claimed in any one of the preceding claims, wherein the amine is a diamine having the formula: 40



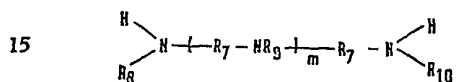
wherein R_3 is a divalent alkylene group having from 1 to 6 carbon atoms, and R_4 and R_5 are an alkyl group having from 1 to 6 carbon atoms or a group having the formula:



wherein R_6 is a divalent alkylene group having from 1 to 6 carbon atoms, and X is a hydroxyl or an amine group.

8. A composition as claimed in claim 7, wherein the diamine is N,N -dimethyl-1,3-propanediamine.

9. A composition as claimed in any one of claims 1 to 6, wherein the amine is an alkylene polyamine of the formula:

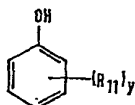


wherein R_8 , R_9 and R_{10} are hydrogen or an alkyl group having from 1 to 4 carbon atoms, and R_7 is a divalent saturated aliphatic hydrocarbon group having from 2 to 4 carbon atoms and m is 0 or an integer of from 1 to 4.

10. A composition as claimed in claim 9, wherein the alkylene polyamine is ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine or a mixture thereof.

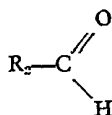
11. A composition as claimed in claim 1, wherein the detergent additive is the reaction product of:

- 30 (i) one mole of phenol or a lower (C_2-C_4) alkyl phenol having the formula



wherein y is 1 or 2, and R_{11} is lower (C_2-C_4) alkyl;

- 35 (ii) from 1 to 3 moles of an aldehyde having the formula



wherein R_2 is hydrogen or an alkyl group having from 1 to 6 carbon atoms; and

- 40 (iii) from 0.5 to 3 moles of an amine having at least one $R_{12}-N-H$ group wherein

R_{12} is an alkyl group having 30 or more carbon atoms.

12. A composition as claimed in claim 11, wherein the amine is a monoamine.

13. A composition as claimed in claim 11, wherein the amine is a polyamine.

14. A composition as claimed in claim 11, wherein the amine is derived from a polymer of a C_2 to C_4 monomer and the polymer has an average molecular weight of 400 to 1500.

15. A composition as claimed in claim 14, wherein the polymer is polypropylene or polybutene.

16. A composition as claimed in any one of the preceding claims, wherein the aldehyde is formaldehyde.

17. A composition as claimed in any one of claims 1 to 15 wherein the aldehyde is paraformaldehyde.

18. A composition as claimed in claim 1, wherein the detergent additive is the reaction product of about 2 mole parts of a polybutene-substituted phenol wherein the polybutene substituent has an average molecular weight of from 900 to 1100, about 3 mole parts of formaldehyde and about 2 mole parts of N,N -dimethyl-1,3-propanediamine.

19. A composition as claimed in claim 1, wherein the detergent additive is substantially as hereinbefore described with reference to any one of Examples 1 to 4.

20. A composition as claimed in any one of the preceding claims which includes a mineral lubricating oil.

21. A composition as claimed in claim 20, wherein the oil is present in an amount of from 0.05 to 0.5 volume percent.

22. A composition as claimed in claim 20 or claim 21, wherein the oil is a naphthenic oil.

23. A composition as claimed in any one of the preceding claims which includes a normally liquid polyolefin oligomer having an average molecular weight of from 300 to 2000.

24. A composition as claimed in claim 23, wherein the polyolefin is present in an amount of from 0.05 to 0.5 volume percent.

25. A composition as claimed in claim 23 or claim 24, wherein the polyolefin has an average molecular weight of from 350 to 1500 and is one made by the oligomerization of a mixture of aliphatic monoolefins having from 12 to 32 carbon atoms.

26. A composition as claimed in claim 23 or claim 24, wherein the polyolefin is substantially as hereinbefore described with reference to any one of Examples 5 to 9.

27. A composition as claimed in any one of the preceding claims which contains from 3 to 1000 ppm of detergent additive.

28. A composition as claimed in claim 1 and substantially as hereinbefore described specifically.

29. A composition as claimed in claim 1

and substantially as hereinbefore described in Table 7.

- 5 30. A gasoline additive concentrate, which concentrate comprises from 0.1 to 90 percent by weight of a detergent additive as defined in any one of claims 1 to 19 and a diluent which is an aliphatic solvent, an aromatic solvent, or a normally liquid aliphatic hydrocarbon oligomer having a molecular weight of
10 from 300 to 2000, or a mixture thereof.

31. A concentrate as claimed in claim 30, wherein the detergent additive is present in an amount of from 10 to 90 percent by weight.

32. A concentrate as claimed in claim 30 and substantially as hereinbefore described specifically. 15

33. A concentrate as claimed in claim 30 and substantially as hereinbefore described in Table 6.

BOULT, WADE & TENNANT.

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